

Relevance of BFRs and thermal conditions on the formation pathways of brominated and brominated–chlorinated dibenzodioxins and dibenzofurans

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Abstract

The widespread use of brominated flame-retarded products in the last two decades has resulted in an increasing presence of bromine in thermal processes such as waste combustion and accidental fires. Brominated and brominated–chlorinated dibenzodioxins and dibenzofurans (PBDDs/PBDFs, PXDDs/PXDFs) are micropollutants of concern arising from such processes. The present review aims to evaluate the relevance of these compound classes in actual thermal processes. Four categories of thermal processes are discussed in this respect according to their potential for PBDD/PBDF and PXDD/PXDF generation: thermal stress, pyrolysis/gasification, insufficient combustion conditions and controlled combustion conditions. Under thermal stress situations, as they may occur in production or recycling processes, PBDDs/PBDFs precursors like polybrominated diphenylethers (PBDE) can have a relevant potential for PBDD/PBDF formation via a simple elimination. Under insufficient combustion conditions as they are present in, e.g. accidental fires and uncontrolled burning as well as gasification/pyrolysis processes, considerable amounts of PBDDs/PBDFs can be formed from BFRs, preferably via the precursor pathway. In contrast, under controlled combustion conditions, BFRs and PBDDs/PBDFs can be destroyed with high efficiency. The relevance of de novo synthesis of PXDDs/PXDFs is discussed for this condition.

Providing a basis for the understanding of PXDD/PXDF formation in actual thermal processes, the present paper also summarises the formation pathways of brominated and brominated–chlorinated PXDDs/PXDFs from brominated flame retardants (BFRs) investigated during laboratory thermolysis experiments. Relevant mechanistic steps for PBDD/PBDF formation from brominated precursors are discussed including elimination reactions, condensation steps and debromination/hydrogenation reactions.

In addition, chlorination/bromination and halogen exchange reactions are briefly discussed with respect for their relevance on the final distribution of PBDDs/PBDFs, mixed chlorinated PXDDs/PXDFs and PCDDs/PCDFs resulting from thermal processes.

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1. Introduction

The increased use of brominated flame retardants (BFRs) in consumer products (such as in electrical equipment like computers and televisions, in furniture, upholstery, plastic heat insulation, building foams, flooring and curtains, etc.) during the last two decades has resulted in the ubiquitous presence of bromine in private housing, offices or public buildings. Although the use of BFR secures an overall

higher fire safety, the presence of brominated compounds during accidental fires may result in the formation of elevated levels of undesirable by-products. The widespread use of brominated flame-retarded products in recent years will also lead to increasing bromine concentrations in waste streams (e.g. plastic waste from electrical and electronic equipment (WEEE)) and hence, brominated compounds are expected to be an increasingly relevant issue in thermal waste treatment.

Bumb et al. (1980) demonstrated in their theory of the “trace chemistry of fire” that polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are formed as trace compounds during combustion processes in the presence of chlorine. The

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Table 1

Comparison of standard reduction potential, bond strength, Van der Waals radii and other properties of chlorine and bromine

	Electronegativity	Standard reduction potential °E at 25 °C (V)	Bond strength (kJ/mol)	Bond strength (kJ/mol)	Van der Waals radii (Å)	Valence	b.p. (°C)	m.p. (°C)
Chlorine	3.0	$\text{Cl}_2(\text{g}) + 2\text{e}^- \leftrightarrow 2\text{Cl}^-$ 1.358	Cl–Cl (242.9); Cl–Cu (382.8)	CH_3 (351.5) C_6H_5 (397.5) $\text{C}_6\text{H}_5\text{CH}_2$ (288.7)	1.8	– 1, 1, 3, 5 or 7	– 34.6	– 100.98
Bromine	2.8	$\text{Br}_2(\text{l}) + 2\text{e}^- \leftrightarrow 2\text{Br}^-$ 1.066	Br–Br (193.9); Br–Cu (331); Br–Cl (218.8)	CH_3 (292.9) C_6H_5 (334.7) $\text{C}_6\text{H}_5\text{CH}_2$ (230.1)	1.95	– 1, 1, 3, 5 or 7	+ 58.78	– 7.2

similar chemical properties of chlorine and bromine (Table 1) suggest that the two elements behave comparably during thermal processes.

The formation mechanisms of PCDDs/PCDFs during thermal processes has been investigated during the last two decades in numerous laboratory studies and under different conditions of combustion (reviewed by Addink and Olie, 1995; Huang and Buekens, 1995; Ballschmiter and Bacher, 1996). It was demonstrated that PCDDs/PCDFs can be formed (a) via de novo synthesis during fly ash catalysed degradation of unburned carbon species (including PAHs, soot, etc.) or (b) from precursor compounds (chlorinated phenols, diphenylethers, phenoxyphenols, biphenyls, etc.) during condensation and/or elimination reactions. In waste incineration processes, chlorine is introduced mainly as inorganic chloride (e.g. NaCl in the organic waste fraction) and from polyvinylchloride (PVC). The precursor pathway is therefore of minor relevance for the formation of PCDDs/PCDFs in most combustion processes.¹ In waste incinerators, PCDDs/PCDFs are formed primarily in the cooling zone via de novo synthesis (Huang and Buekens, 1995).

In contrast, bromine is primarily present in specific plastics in the form of BFRs specifically brominated aromatic compounds which can act as precursors for PBDDs/PBDFs formation (e.g. brominated diphenylethers (PBDEs) or brominated phenols (PBP)). Hence, the precursor pathway is of higher relevance for the formation of PBDDs/PBDFs during thermal processes compared to their chlorinated analogues.

This paper represents an overview on the formation pathways of PBDDs/PBDFs from brominated precursors, and reviews the relevance of the precursor pathway and other reaction steps in the formation of PBDDs/PBDFs and mixed brominated–chlorinated PXDDs/PXDFs during thermal processes. For a systematic approach, it is important to distinguish different thermal conditions and their impact on condensation reactions of the precursors or their destruction. Since chlorine is typically present in most thermal processes at higher concentrations compared to bromine, halogen exchange reactions are also discussed.

1.1. Formation of PBDDs/PBDFs during laboratory thermolysis experiments of brominated aromatic flame retardants

Numerous studies have shown that the thermolysis of certain brominated flame retardants results in the formation of PBDDs/PBDFs (Table 2). In particular, experiments using brominated aromatics that could be considered as PBDD/PBDF precursors² (PBDEs, PBBs or PBP) resulted in high yields of PBDDs/PBDFs (Table 2). The following section of this paper discusses potential precursors, their differences in the PBDD/PBDF formation pathways and their PBDD/PBDF formation potential.

1.1.1. Thermal conversion of polybrominated diphenylether³ to PBDDs/PBDFs—relevance of elimination and debromination reactions (Fig. 1)

Large yields of PBDDs/PBDFs were reported from thermolysis of PBDEs with values up to the percentage range (Thoma et al., 1987a,b,c; Dumler et al., 1989a,b, 1990; Buser 1986a; Zacharewski et al., 1988; Luijk et al., 1991) (Table 2). The presence of a polymer matrix (Thoma et al., 1987a; Dumler et al., 1990) and Sb_2O_3 (Clausen et al., 1987; Bieniek et al., 1989; Dumler et al., 1989a, 1990; Luijk et al., 1991) increased the yield of PBDDs/PBDFs formed and decreased the optimum temperature range (Table 2).

From a mechanistic point of view, the formation of PBDFs from PBDEs requires only an intra-molecular elimination of Br_2 or HBr (Fig. 1). It is generally observed that the yield of PBDD/PBDFs in pyrolytic residues decreases from pentaBDEs,⁴ octaBDEs to decaBDEs (Buser, 1986a; Thoma et al., 1987a; Luijk et al., 1991) (Table 2). Luijk et al. (1991) suggested that the higher yield of PBDFs from low brominated PBDEs is due to the energetically favourable elimination of HBr in lower brominated DPE (requirement of an hydrogen position in *ortho*-position of the

¹ Except for processes where, e.g. PCBs or chlorophenols are present in high concentration (e.g. transformer fires, combustion of PCP treated wood).

² Precursors are halogenated aromatic compounds which by a simple condensation or elimination step can be transformed into PXDDs/PXDFs.

³ Pyrolysis experiments involving PBDEs were summarised in an Environmental Health Criteria monograph (WHO, 1994).

⁴ PentaBDEs have been phased out in Europe and Japan. It is however difficult to estimate their presence in waste plastics.

Table 2

Formation of PBDD and PBDF in some laboratory thermolysis experiments with brominated flame retardants

Brominated flame retardant	Polymer (additive)	Condition of thermolysis	Maximum yields (ppm) (homologues)	Reference
<i>PBDE</i>				
Technical PBDE	none	quartz vials, air, 630 °C	ΣPBDF/D 100000 (Br ₁ –Br ₆)	Buser, 1986a
Technical OBDE	none	quartz vials, air, 630 °C	ΣPBDF/D 50000 (Br ₃ –Br ₇)	Buser, 1986a
Technical DCB	none	quartz vials, air, 630 °C	ΣPBDF/D 10000 (Br ₄ –Br ₈)	Buser, 1986a
Technical PBDE	none	quartz vials 600 °C	ΣPBDF/D 270000 (Br ₄ –Br ₆)	Luijk et al., 1991
Technical OBDE	none	quartz vials 600 °C	ΣPBDF/D 56000 (Br ₄ –Br ₆)	Luijk et al., 1991
Technical DBDE	none	quartz vials 600 °C	ΣPBDF/D 1700 (Br ₄ –Br ₆)	Luijk et al., 1991
Technical PBDE	none	quartz tubes 700–900 °C	ΣPBDD 330400 (Br ₁ –Br ₅) (700 °C) ΣPBDD 15400 (Br ₁ –Br ₄) (700 °C)	Thoma et al., 1987a
Technical DBDE	none	quartz tubes 700–900 °C	ΣPBDF/D 13413 (Br ₅ –Br ₈) (900 °C)	Thoma et al., 1987a
Technical DBDE	none	DIN-oven 400–800 °C	400 °C ΣPBDF 410 (Br ₆ –Br ₈) 600 °C ΣPBDF 2760 (Br ₆ –Br ₈)	Dumler et al., 1990
Technical DBDE	PBT	DIN-oven 400–800 °C	400 °C ΣPBDF 15000 (Br ₁ –Br ₇) 600 °C ΣPBDF 26000 (Br ₁ –Br ₇)	Dumler et al., 1990
Technical DBDE	PBT + Sb ₂ O ₃	DIN-oven 400–800 °C	400 °C ΣPBDF 105000 (Br ₁ –Br ₇) 600 °C ΣPBDF 18000 (Br ₁ –Br ₇)	Dumler et al., 1990
<i>PBP</i>				
2-MBP	none	ovens (BIS, DIN, VCI) 600 °C	ΣPBDD 60634 (Br ₁ –Br ₂) ΣPBDF 215425 (Br ₁ –Br ₃)	Hutzinger et al., 1989
2,4,6-T3BP	none	ovens (BIS, DIN, VCI) 600 °C	ΣPBDD 896000 (Br ₂ –Br ₆) ΣPBDF 8950 (Br ₃ –Br ₅)	Hutzinger et al., 1989
P5BP	none	ovens (BIS, DIN, VCI) 600 °C	ΣPBDD 3567 (Br ₄ –Br ₇) ΣPBDF 3307 (Br ₃ –Br ₄)	Hutzinger et al., 1989
2,4,6-T3BP	none	flow reactor 300–800 °C	ΣPBDD 510000 (Br ₄) (500 °C)	Sidhu et al., 1995
2,4-DBP + 2,4-DCP	none	quartz vials 300	ΣPXDD 10000 (X ₁ –X ₄)	Sakurai and Weber, 2002
<i>PBBs</i>				
Technical HexaBB (FM BP-1)	none	glass tubes	ΣPBDF 44 (Br ₄ –Br ₅)	O'Keefe, 1987
Technical HexaBB (FM BP-6)	none	quartz tube 800 °C	ΣPBDF 2070 (Br ₃ –Br ₇)	Zacharewski et al., 1988
Technical HexaBB (FM BP-6)	PS	quartz tube 700, 800, 900 °C	ΣPBDF 8900 (Br ₁ –Br ₄)	Thoma et al., 1987a,b,c
DecaBB	PE	quartz tube reactor 400–700 °C	ΣPBDF 43000 (Br ₁ –Br ₄)	
	PBT	quartz tube reactor 400–700 °C	ΣPBDF 100 (Br ₃ –Br ₈)	Luijk and Govers, 1992
<i>TBBP-A and derivatives</i>				
TBBP-A	none	quartz tubes 700, 800 and 900 °C	ΣPBDD 498 (Br ₁ –Br ₄) ΣPBDF 1150 (Br ₁ –Br ₄)	Thoma et al., 1986
TBBP-A	none	oven 600 °C	ΣPBDD 116 ΣPBDF 99	Dettmer, 2001
TBBP-S	none	oven 600 °C	ΣPBDD 2090 ΣPBDF 260	Dettmer, 2001
TBBP-A	various	ovens (BIS, DIN, VCI) 600–800 °C	ΣPBDD/F (Br ₁ –Br ₃) few ppm	Dumler et al., 1989b

PBDEs (Fig. 1)), compared to the energetically less favourable elimination of two bromine substituents in highly brominated DE. An alternative explanation for the low PBDD/PBDF formation potential of higher brominated PBDEs may be the steric hindrance in the formation of CC bond, when bromine substitution results in 1,9-substituted PBDF: the bromine substituents in 1,9 position in PBDFs cause a “steric crowding” (Fig. 1). Therefore, the formation of PBDFs with a hydrogen substituent in 9-position is favoured (requirement of a hydrogen position in meta-position of PBDEs (Fig. 1)). The effect of steric crowding of 1,9-halogenation has been reported for the

chlorinated OCDF⁵ (Hileman et al., 1989; Weber et al., 2002a). For brominated PBDFs, this steric effect is expected to have an even larger impact compared to PCDFs due to the larger Van der Waals radius of Br compared to Cl (Table 1). Both mechanistic explanations emphasise the importance of hydrogen substituents for the formation of PBDFs from PBDEs.

The debromination/hydrogenation reactions therefore play a key role in the transformation of the fully brominated

⁵ The isomer pattern of PCDF in thermal processes is therefore characterised by the lack of 1,9-substituted congeners.

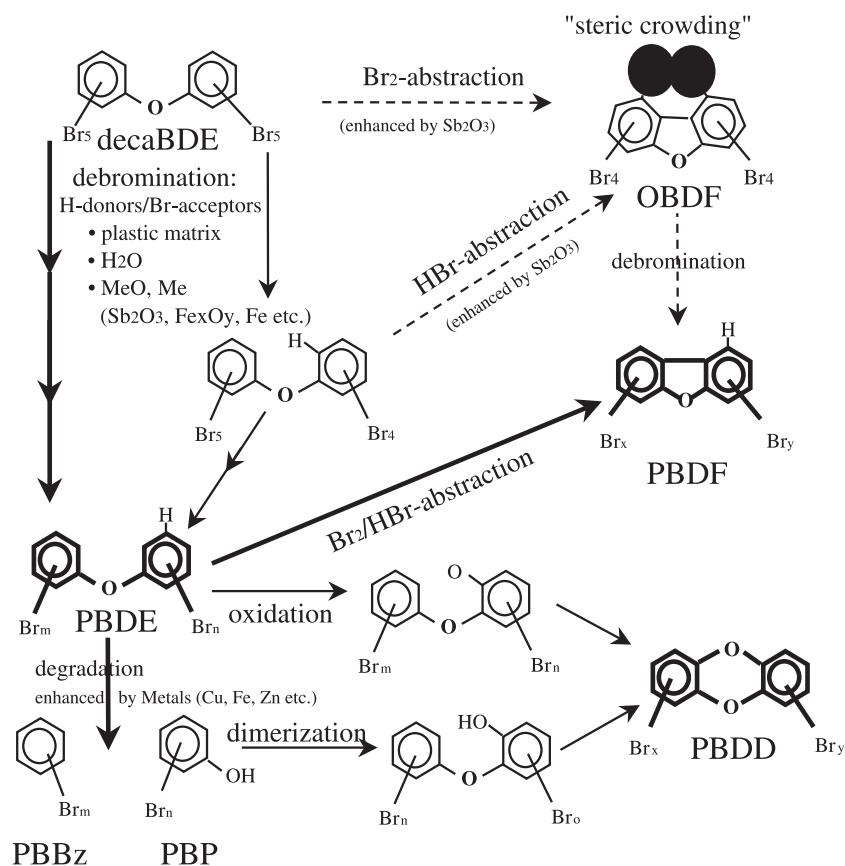


Fig. 1. Formation pathways of PBDDs and PBDFs from decaBDE during thermal degradation.

decaBDE to PBDFs. Debromination reactions are generally observed during thermal degradation of polybrominated aromatics above 500 °C (Striebich et al., 1991; Luijk et al., 1992). Various factors can increase the rate and decrease the on-set temperature of the debromination/hydrogenation reaction.

- The presence of a polymer matrix serves as hydrogen donor during thermal degradation shifting the homologue pattern to lower brominated congeners and enhancing PBDF formation significantly (Dumler et al., 1990) (Table 2). In this respect, Luijk et al. (1992) reported on a debromination of decaBDE already in the polymer melting phase and the abstraction of hydrogens from the polymer backbone.
- A further increase in PBDF yield results when Sb₂O₃ is added to the decaBDE/polymer (Dumler et al., 1990) (Table 2). The addition of Fe₂O₃ as well significantly enhanced the condensation of decaBDE to PBDFs (Lenoir et al., 1994). These metal oxides can catalyse the debromination/hydrogenation reaction.⁶ In addition, they also may catalyse the elimination of HBr/Br₂ in the

condensation step (e.g. by formation of SbO_xBr_y (Dumler et al., 1990).

- The presence of water is a third factor increasing the formation rate of PBDFs from decaBDE (Zier et al., 1991; Lenoir et al., 1994). This observation can be explained by a positive effect of water on dehalogenation/hydrogenation reactions. Such an influence of water on dehalogenation/hydrogenation of chlorinated aromatics has been reported for the dechlorination of PCDDs/PCDFs (Hagenmaier et al., 1987).

To date, a systematic investigation of the thermal debromination has not been performed. Due to the relevance of the debromination/hydrogenation reaction for the transformation of highly brominated DEs to PBDFs, it would be important to gain a better understanding of these processes.

PBDDs have also been found to form during thermolysis of PBDEs. However, the yields were considerably lower compared to PBDFs in most cases investigated (Dumler et al., 1990b; Luijk and Govers, 1992). The formation of PBDDs from decaBDE in polybutylene terephthalate (500 °C, BIS furnace) were increased when metals such as tin, iron, zinc or copper were present and could then even surmount the amount of PBDFs formed (Lenoir et al., 1994). An intra-molecular oxygen insertion was proposed as mechanism for PBDD formation from PBDEs by Buser

⁶ The catalytic effect of various metal oxides on dehalogenation/hydrogenation was shown for chlorinated aromatic compounds on model fly ashes (Weber et al., 2002c).

(1986b) and Luijk et al. (1991) (Fig. 1). In contrast, Lenoir et al. (1994) proposed PBDEs molecules degrade to form polybrominated phenols (PBP) and polybrominated benzenes (PBBz) followed by a dimerisation of PBP (Fig. 1). The formation of PBDDs from PBDEs via the bromophenol pathway is supported by the positive effect of metals and their mechanistic implications (Lenoir et al., 1994).

1.1.2. Thermal conversion of polybrominated biphenyls (PBBs) to PBDFs—relevance of oxygen insertion

The pyrolysis of brominated biphenyls results in the formation of PBDFs in concentrations up to approximately 2000 µg/g (O'Keefe, 1987; Zacharewski et al., 1988; Thoma and Hutzinger, 1989) (Table 2). The presence of plastic matrices during this process results in an increased formation yield and lower brominated PBDF homologues (Table 2: compare Thoma et al., 1987a,b,c and Zacharewski et al., 1988). The yields are however low compared to the formation of PCDFs from PCBs where yields were found in the percent range (Buser et al., 1978). However, thermolysis experiments with PBBs were performed either at rather high temperatures of 700–900 °C (Thoma et al., 1987a,b,c; Zacharewski et al., 1988) or at low temperatures of 380–400 °C (O'Keefe, 1987) (Table 2). The optimum temperature range of 500–700 °C, where high yields of PCDF from PCB are formed (Buser et al., 1978), were not investigated.

From a mechanistic point of view, the formation of PBDFs from PBBs require only an oxygen insertion. Luijk et al. (1992) concluded that the formation of PBDFs from decaBB in polybutylene terephthalate includes condensed phase and gas phase mechanisms for the oxygen insertion. Detailed mechanisms were not discussed in other studies. Buser and Rappe (1979) investigated the formation pathways of PCDF from single PCB isomers during thermal degradation. These authors demonstrated that PCDFs were formed by intra-molecular cyclisation involving either abstraction of HCl, two chlorine or two hydrogen substitu-

ents during oxygen insertion (Buser and Rappe, 1979). Due to the similar chemical properties of chlorine and bromine substituents (Table 1), it can be assumed that the formation mechanisms of PBDFs from PBBs are comparable to the reaction routes of PCDFs from PCBs. The small differences in, for example, the binding energy (Table 1) are expected to result in a (minor) shift in the preferred elimination steps or in the temperature optimum. Investigations with single PBB isomers would be necessary to elucidate the detailed mechanism.

1.1.3. Thermal conversion of bromophenols to PBDD/PBDF—relevance of condensation reactions (Fig. 2)

Brominated phenols show a high potential for the formation of PBDDs/PBDFs during thermolysis (Hutzinger et al., 1989; Sidhu et al., 1995; Sakurai and Weber, 2002). Sidhu et al. (1995) and Hutzinger et al. (1989) reported formation yields of 56% (500 °C) and 89% (600 °C) during thermolysis of 2,4,6-triBP, respectively (Table 2). Sakurai and Weber (2002) investigated the PBDD/PBDF formation mechanism from 2,4-diBP at low temperature (300 °C). In the first condensation step (formation of the phenoxyphe- nol), bromine or hydrogen can be substituted (Fig. 2). In the second condensation step, bromine is eliminated with a high selectivity (Fig. 2).

Above ca. 350 °C, PBDFs are formed additionally from bromophenols containing a hydrogen substituent in *ortho*-position analogous to the formation of PCDFs from chlorinated phenol (Fig. 2; Weber and Hagenmaier, 1999). At higher temperatures, PBDFs can also be formed from bromophenols with bromine substitution in both *ortho*-positions (Thoma et al., 1986; Hutzinger et al., 1989) (Table 2). However, at 800 °C and a residence time of 2 s, 2,4,6-triBP has been shown to be destroyed to concentrations below the detection limit and no PBDDs/PBDFs were formed (Striebig et al., 1991).

Sidhu et al. (1995) and Sakurai and Weber (2002) reported that the brominated phenols show a higher poten-

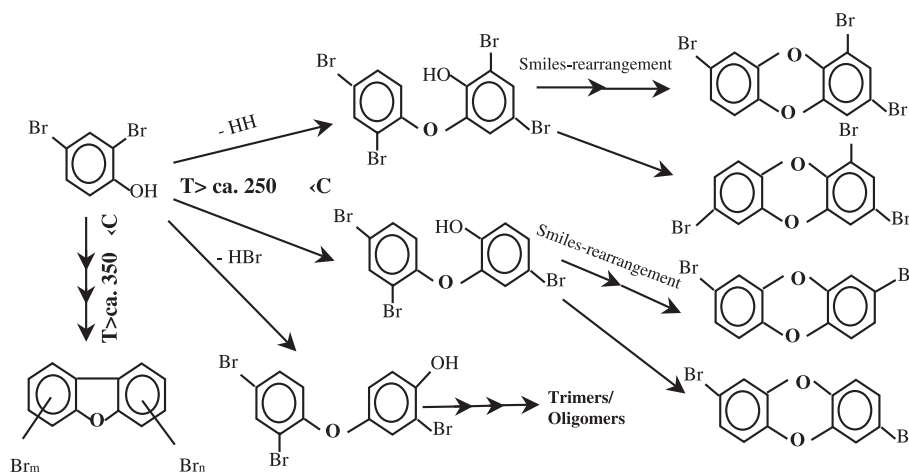


Fig. 2. Formation of PBDDs and PBDFs from 2,4-dibromophenol.

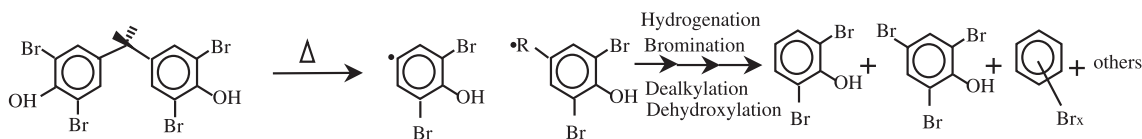


Fig. 3. Thermal degradation of TBBP-A and formation of bromophenols and bromobenzenes.

tial in the formation of PXDDs/PXDFs compared to their chlorinated analogues. Bromine is more easily substituted, which can be explained by the lower binding energy of the brominecarbon bond compared to the chlorinecarbon bond (Table 1).

The relevance of bromophenols on the formation of PBDDs/PBDFs is not restricted to their initial presence in a starting material. For example, the formation of bromophenols is observed during thermal degradation of BFRs such as PBDEs (see above, Figs. 1 and 4) or TBBP-A (see below, Figs. 3 and 4). Intermediately formed bromophenols and bromobenzenes can therefore play an important role in the formation of PBDDs/PBDFs during thermal processes (Fig. 4).

1.1.4. Thermal conversion of tetrabromobisphenol-A (TBBP-A) to PBDD/PBDF—the relevance of pre-formation of precursors

For most BFRs, a formation of PBDDs/PBDFs by a simple elimination or condensation step is not possible. TBBP-A, the most widely used BFR, is one example in this respect (Fig. 3). Although formation of PBDDs and PBDFs has been observed during thermolysis of TBBP-A (Thies et al., 1990; Dumler et al., 1989b; Dettmer, 2001; Wichmann et al., 2002), the yields were orders of magnitudes lower compared to PBDEs or bromophenols (Table 2) and only a few ppm of low brominated PBDDs/PBDFs ($\text{Br}_1\text{--Br}_3$) were

generated in the presence of a polymer matrix (Dumler et al., 1989a,b). Wichman et al. (2002) reported that the added TBBP-A and the polymer-linked TBBP-A resulted in comparable amount of PBDDs/PBDFs ($\text{Br}_1\text{--Br}_5$) in the ppm range with a predominant formation of monoBDF. Dettmer (2001) investigated the thermal degradation of TBBP-A and its analogues (TBBP-S, TBBP-S-dibromopropylether and Non Nen #52) during thermal degradation and observed the formation of large amounts of brominated phenols (up to 17%) and to a lesser amount brominated benzenes (up to 0.5%). The amount of brominated phenols and benzenes detected in the condensates showed a good quantitative correlation to the amount of PBDDs and PBDFs formed. The formation of PBDDs/PBDFs from TBBP-A and related flame retardants proceeds therefore, most probably, in two steps (Dettmer, 2001):

- the generation of precursors (PBP and PBBz) during thermal degradation/incineration of the polymer/TBBP-A (Fig. 3) and
- dimerisation/condensation of the precursors (Figs. 2 and 4).

In this respect, it might be interesting to evaluate the potential of BFRs to form brominated phenols (and other precursors) during thermal degradation.

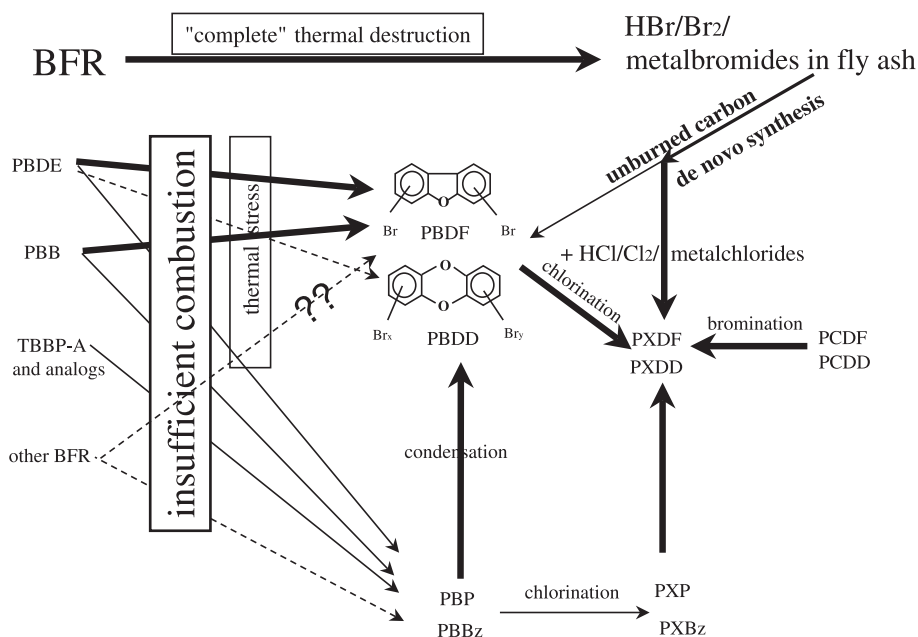


Fig. 4. Formation pathways of PBDDs/PBDFs and PXDDs/PXDFs in thermal processes.

1.2. Presence of bromine and chlorine in thermal processes

In most combustion processes, chlorine concentrations considerably exceed bromine concentrations. On the other hand, bromine can already be present to a large extent as brominated aromatic flame retardants. The final amount of brominated, brominated–chlorinated and chlorinated aromatics therefore depends on chlorination/bromination reactions and halogen exchange reactions.

(a) Bromine–chlorine exchange reactions.

The bromine–chlorine exchange reactions have been observed under various conditions (Thoma et al., 1987a,b, 1989; Zier et al., 1991; Luijk et al., 1994). Luijk et al. (1994) investigated the time and temperature dependence of bromine–chlorine exchange in tetraBDDs with CuCl_2 on $\text{Al}_2\text{O}_3\text{--SiO}_2$. At 250 °C, a measurable exchange of bromine by chlorine was observed within 5 min. Zier et al. (1991) investigated the bromine–chlorine exchange in various brominated aromatics on fly ash from a municipal waste incinerator at 300 °C. A fast ipso substitution of bromine by chlorine was observed, proposing a nucleophilic mechanism for the bromine–chlorine exchange reaction on fly ashes. Thoma et al. (1987a,b) demonstrated that in the presence of a chlorine donor at 800 and 900 °C, extensive bromine–chlorine exchange reactions take place without a catalyst in laboratory pyrolysis experiments, leading to mixed halogenated PXDDs/PXDFs and fully chlorinated PCDDs/PCDFs. The chlorine source could either be organic or inorganic.

Söderström and Marklund (2000) combusted BFRs in a pilot scale incinerator together with standardised MSW containing chlorine and observed the formation of PXDDs/PXDFs. The formed tetraXDFs/tetraXDDs were in agreement with the calculated statistic ratio from molar amounts of bromine and chlorine indicating a fast bromine–chlorine exchange under combustion conditions.

(b) Bromination of PCDDs/PCDFs.

The possibility of bromination of PCDDs/PCDFs in the cooling line of an incinerator was suggested by Huang et al. (1992) and Sovocool et al. (1989) particularly when fly ash moves from hotter to cooler regions. The relevance of this pathway is not yet confirmed through experimental studies. Öberg (1989) reported that in hazardous and municipal waste incinerators, a relatively higher yield of brominated compounds were formed when comparing the input of bromine and chlorine which might indicate a relevance of bromination reaction under these conditions. More research is necessary to evaluate the impact of bromination reactions in this respect.

(c) Bromine and chlorine is incorporated in parallel during de novo synthesis of PXDDs/PXDFs (see below, Section 1.3.4.3).

In de novo synthesis, experiments on model fly ashes containing bromine and chlorine, mixed chlorinated–brominated PXDDs and PXDFs are formed (Weber et al., 2002b), suggesting that bromine and chlorine is substituted in parallel when present in fly ashes. The authors concluded that the ratio of substituted chlorine/bromine depends—in addition to

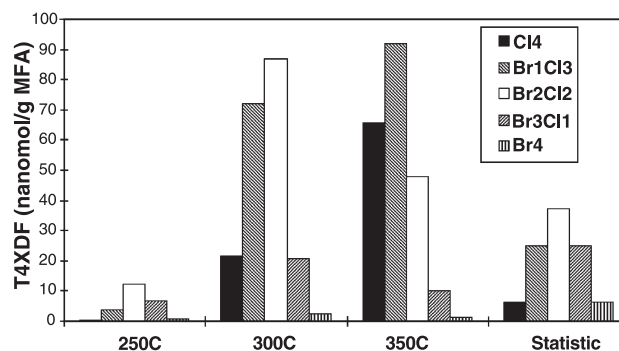


Fig. 5. Distribution of tetrahalogenated dibenzofurans in the de novo experiments at 250, 300 and 350 °C in comparison to the calculated distribution from the equimolar ratio of the halogens on the model fly ash. (model fly ash on silica base, 0.5% $\text{Cu}(\text{OH})_2$; 1%Cl and 2.2%Br (as KX), 0.2% perylene, 30 min, Pyrex vials).

the bromine and chlorine content of the ash—also on the temperature and residence time (Fig. 5).

A better understanding of chlorination and bromination reactions under the respective conditions would be one step towards a crude estimation of the impact of mixed halogenated PXDDs/PXDFs in combustion processes or accidental fires. However, one difficulty in this respect is the estimation of the quantity of chlorine and bromine present in the respective fire/combustion processes.

1.3. Formation of PBDDs/PBDFs during actual thermal processes

In addition to the molecular structure of BFRs, the reaction conditions have a fundamental impact on the amount of PBDDs/PBDFs formed. Even the thermolysis in different types of ovens (DIN-oven, BIS-oven and VCI-oven) of a single BFR at the same temperature can have a significant impact on PBDD/PBDF formation rates (Dumler et al., 1989b). This has to be considered when actual thermal processes are evaluated for their PBDD/PBDF formation potential.

For a simplification, the thermal processes are discussed within the following four categories⁷ (Table 3):

- thermal stress,
- pyrolysis/gasification processes,
- insufficient combustion/fires and
- controlled combustion conditions

1.3.1. Formation of PBDDs/PBDFs during thermal stress—production, processing and recycling of brominated flame-retarded plastics⁸

A formation of PBDFs from PBDEs has been observed even under the mild thermal stress of production steps of

⁷ Real thermal/combustion processes may include more than one of these categories.

⁸ For a detailed description of this subject, see the paper of Ebert and Bahadir (2003).

Table 3

Categories of thermal treatment, related actual processes, prevailing formation pathways and potential of PBDD/PBDF and PXDD/PXDF formation

Category	Processes	Conditions	Prevailing formation pathways	PXDD/PXDF formation potential
Thermal stress	production (extrusion, molding) recycling	100–300 °C, mechanical stress	selected precursors (e.g. PBDE)	low-moderate
Pyrolysis/gasification	pyrolysis/gasification facilities (pyrolysis of plastics, shredder fractions or sludges)	350–800 °C, low oxygen	precursors; + formation of aromatic compounds and halogenation, (+ de novo synthesis)	high
Insufficient combustion conditions	accidental fires, uncontrolled burning, “uncontrolled” incinerators	uncontrolled: temperature; residence time; oxygen supply, turbulence	precursors; (+ de novo synthesis)	high
Controlled combustion conditions	state of art incinerators	optimised combustion control	de novo synthesis in cooling zone	low

plastics like extrusion or moulding (Luijk et al., 1992; Donnelly et al., 1989; McAllister et al., 1990). Factors influencing the extent of PBDDs/PBDFs formation include temperature and duration of the process (Donnelly et al., 1989; McAllister et al., 1990). The presence of a precursor such as PBDEs that can form PBDFs via a simple elimination step (Fig. 1) appears to be a prerequisite for PBDF formation (Fig. 4). No PBDDs/PBDFs formation could be observed during production processes in the presence of BFRs which are not direct precursors such as brominated styrene or brominated phenoxyethan (Bonilla et al., 1990).

Another thermal stress situation for polymers may occur during recycling processes. However, relevant formation of PBDDs/PBDFs was not observed from TBBP-A containing printed circuit boards during thermal and mechanical stress in recycling processes involving hammer mill, impact grinder or granulation process (Lorenz and Bahadir, 1993). Furthermore, Meyer et al. (1993) did not observe significant amounts of PBDDs/PBDFs in plastic scrap containing TBBP-A, even after several recycling cycles. In scrap plastic containing PBDE, however, elevated concentrations of PBDDs/PBDFs, including 2,3,7,8-substituted PBDDs/PBDFs, were detected (Meyer et al., 1993). The authors concluded that plastics containing PBDEs can therefore not be recycled and that the type of flame retardants used determines the recyclability (Meyer et al., 1993).

The precursor potential of BFRs to form PBDDs/PBDFs is therefore a key factor for thermal stress situations in production or recycling processes. Since the diversity of BFRs has increased in recent years, an evaluation of the various BFRs presently in use would be necessary for a detailed assessment.

1.3.2. Formation of PBDDs/PBDFs in pyrolysis/gasification processes

In recent years, pyrolysis and gasification processes have been technologically developed to industrial scale and are discussed as alternatives to the existing waste combustion processes.

The behaviour of BFRs and PBDDs/PBDFs in pyrolysis/gasification plants processing brominated flame-retarded plastic materials has not been reported to date. Considering the results from laboratory thermolysis (Thoma et al., 1987a; Clausen et al., 1987; Dumler et al., 1989a, 1990; Buser, 1986a; Zacharewski et al., 1988; Luijk et al., 1991; Bieniek et al., 1989), however, elevated concentrations of PBDDs/PBDFs may be expected from pyrolysis/gasification processes depending on the type of BFR present in the waste.

The pyrolysis of shredder waste containing a high amount of chlorine (PVC) and metals (iron and copper) has been shown to result in the formation of high levels of chlorinated aromatics including PCDDs/PCDFs (Rosemann et al., 1998; Weber and Sakurai, 2001).⁹ Therefore, the formation of aromatic compounds and halogenation processes may additionally result in the formation of PXDDs/PXDFs and not necessarily depend on the type of BFR.

The treatment of municipal waste, using pyrolysis or gasification processes, is typically combined with a high temperature melting treatment (Thomé-Kozmiensky, 1994). Sakai (2000) demonstrated that melting processes result in a high destruction efficiency of PBDDs/PBDFs (>99.9%) as well as of BFRs. Therefore, pyrolysis/gasification processes in combination with a melting step may represent an appropriate method for the processing of flame-retarded plastic waste.

1.3.3. Formation of PXDDs/PXDFs during insufficient combustion—fire simulation, accidental fires and uncontrolled waste burning

In experimental fire tests simulating real fire conditions, high PBDDs/PBDFs concentrations were found to result from combustion of television sets (Fabarius et al., 1990) and electrical appliances/casing parts of electrical appliances (UBA, 1992). The total PBDD/PBDF concentrations in combustion residues reached values between 1 and 9000

⁹ The PCDDs/PCDFs could be destroyed in an additional incineration step (Weber and Sakurai 2001).

µg/g. Their concentration in the smoke samples ranged between 0.8 and 1700 µg/m⁻³. (Fabarius et al., 1990; UBA, 1992) with PBDD concentrations less than 3% of total PBDDs/PBDFs. Maximum values were found for tri- to hexaBDD/BDF.

In accidental fires, PBDDs/PBDFs were detected at concentrations predominantly below those found in the fire simulation experiments (Buser, 1986b; Fabarius et al., 1990; Bruckmann et al., 1990; Zelinski et al., 1993). However, the qualitative composition of the samples was similar. The PBDF levels of the accidental fire combustion residues were mainly in the ng/g range. In some cases, however, elevated concentrations of up to 107 µg/g (UBA, 1992) and 34 µg/g PBDFs (Zelinski et al., 1993) have been observed.

For PCDD/PCDF, it was demonstrated that uncontrolled burning of domestic waste can result in high levels of PCDDs/PCDFs (Gullett et al., 2000). An uncontrolled burning of waste containing brominated flame retardants (e.g. WEEE) seems even more critical. Therefore, the practice of uncontrolled burning of WEEE, e.g. for metal recycling purposes (Basel Action Network, 2003) should be critically evaluated in this respect.

Even in incineration plants, insufficient combustion conditions can cause an incomplete destruction of halogenated aromatic compounds and such compounds can also be formed again (Hunsinger et al., 2002). Therefore, BFRs can act as precursors to form PBDDs/PBDFs and PXDDs/PXDFs under such conditions.

The flame retardants included in the materials used for the fire simulations and present in the accidental fires mentioned above were mostly unknown.¹⁰ Therefore, formation pathways could not be further investigated. It can be assumed, however, that under insufficient combustion conditions and in the presence of BFRs, the formation pathways are similar to those determined for thermolysis experiments. In this case, formation of PBDDs/PBDFs from precursors most likely represents the key pathway under these conditions (Figs. 1–4). The high concentrations of PBDFs found in accidental fire investigations may indicate that primarily brominated diphenylethers were available as precursors and that phenolic compounds (generally associated also with PCDD formation in thermolysis reactions (Table 2)), played only a minor role. In this respect, fire simulations with plastics containing known flame retardants could provide more insight into the role of BFRs to PBDDs/PBDFs formation under insufficient combustion conditions.

1.3.4. Formation and destruction of PXDDs/PXDFs under controlled combustion conditions

1.3.4.1. Destruction of halogenated aromatics during combustion. It has been shown that the PCDDs/PCDFs (and other chlorinated aromatics) present in the waste

stream or formed in the fuel bed (Hunsinger et al., 2002) can be destroyed under controlled secondary combustion conditions (temperatures above 850 °C,¹¹ residence time of at least 2 s, and sufficient turbulence for mixing oxygen and gas in the combustion area) (Hagenmaier, 1991). Due to the less stable brominecarbon bond (Table 1), brominated aromatics can be expected to be destroyed faster in thermal processes compared to their chlorinated analogues. In laboratory experiments, it was demonstrated that under oxidative conditions comparable to incineration, brominated precursors such as 2,4,6-triBP or PBDEs can be destroyed at 800 °C and 2-s residence time without formation of PBDDs/PBDFs (Striebich et al., 1991).

Sakai et al. (2001) demonstrated a high destruction efficiency of BFRs in a laboratory scale incinerator combusting TV casing and waste-printed circuit boards. PBDEs were destroyed by more than 99.9% at a residence time of 2 s. In these tests, PBDDs/PBDFs present in the input materials were decomposed during the incineration process. The overall destruction rate in all runs was more than 90%.¹² For some runs where PBDDs/PBDFs increased during the cooling process, the authors suggested that part of the PBDDs/PBDFs were formed by de novo synthesis.

In another incineration experiment, Vehlow et al. (2000) combusted pre-treated municipal solid waste (containing up to 12 wt.% of different types of electrical and electronic (E+E) waste plastics) in a test incinerator. High levels of HBr were detected in the flue gas (up to 300 mg/nm³). The elevated bromine concentrations resulted in only limited concentrations of brominated–chlorinated PXDDs/PXDFs, and the levels of PCDDs/PCDFs were not altered significantly by the co-combustion of materials containing BFRs. Calculating the mass balance of PBDDs/PBDFs, more than 90%¹² of PBDDs/PBDFs present in the input materials were destroyed in these combustion tests (Vehlow et al., 2000). This indicates that, BFRs can be decomposed with high efficiency under controlled combustion conditions. The precursor pathway is expected to have a low impact for the formation of PXDDs/PXDFs under these conditions whereas the relevance of de novo synthesis should prevail, similar to the formation of the PCDDs/PCDFs in municipal waste incinerators (MWI).

Some studies on MWI reported that an increase in bromine input during test operations resulted in increased levels of PXDDs/PXDFs as well as an increase of PCDDs/PCDFs (Öberg et al., 1987; Wilken et al., 1990; Lahl et al., 1991). The cause of this increased PCDDs/PCDFs, how-

¹⁰ With some exceptions where penta- or decabromodiphenyls were specified.

¹¹ For the destruction of PCB in European hazardous waste incinerators, temperatures of more than 1100 °C are required by law (The European Parliament, 2000).

¹² The destruction efficiency of the combustion process itself is higher considering that the largest part of the PXDDs/PXDFs finally emitted are formed in the cooling process of the flue gas by de novo synthesis.

ever, could not be clarified.¹³ Further research on state of the art incinerators with co-combustion of brominated flame-retarded plastic would be necessary in this respect.

1.3.4.2. Detection of PXDDs/PXDFs in actual municipal waste incinerators. Mixed chlorinated–brominated PXDDs/PXDFs and PBDDs/PBDFs have been detected in municipal, hazardous and clinic waste incineration (Schäfer and Ballschmiter, 1986; Öberg et al., 1987; Harless et al., 1989; Huang et al., 1992; Chatkittikunwong and Creaser, 1994; Watanabe and Sakai, 2001). In a recent emission survey from 75 incineration plants in Japan, the average contribution of mixed chlorinated–brominated PXDDs/PXDFs was 12% of PCDDs/PCDFs (Watanabe and Sakai, 2001). Other studies reported contributions of 1–20% to PCDDs/PCDFs (Sovocool et al., 1989; Harless et al., 1989; Tong, 1991; Chatkittikunwong and Creaser, 1994). Specifically, monobromopolychloroDDs/DFs were detected in all these studies. The isomer distribution patterns for PXDDs/PXDFs were similar to those found for PCDDs/PCDFs and similar among different samples, indicating common formation mechanisms (Harless et al., 1989; Huang et al., 1992; Chatkittikunwong and Creaser, 1994). Similar to the formation of chlorinated PCDDs/PCDFs in municipal waste incinerators, de novo synthesis therefore most likely represents the major pathway in the formation of brominated–chlorinated PXDDs/PXDFs.

1.3.4.3. De novo synthesis of PXDDs/PXDFs. Only few studies investigated the de novo synthesis of PBDDs/PBDFs and PXDDs/PXDFs in the presence of bromide. Heinbuch and Stieglitz (1993) demonstrated that substituting the inorganic chloride by bromide in fly ash from municipal waste incinerators results in a comparable de novo synthesis of brominated aromatic compounds. These authors concluded that bromide acts in the same manner as chloride under the applied de novo conditions.

As mentioned above, the presence of chlorine and bromine in de novo synthesis experiments with model fly ash results in the formation of mixed chlorinated–brominated PXDDs/PXDFs (Weber et al., 2002b). The ratio of bromine and chlorine substitution was shown to depend on the temperature and the residence time. The ratio of bromine substitution decreased as temperatures rose (Fig. 5) and residence time became more prolonged. At 350 °C (and less pronounced at 300 °C), the chlorine content in the PXDDs/PXDFs exceeded the statistically expected chlorine/bromine ratio considerably, considering the equimolar concentration of the two halogens in the model fly ash. However, at 250 °C, the bromine content slightly exceeded the statistically expected ratio (Fig. 5). The isomer patterns of chlorinated, brominated–chlorinated and brominated PXDDs and PXDFs in the de novo experiments

were similar, suggesting that the substitution mechanism of bromine and chlorine during de novo synthesis is also similar (Weber et al., 2002b).

2. Conclusions

The similar chemical properties of bromine and chlorine result in similar formation behaviours of PXDDs/PXDFs from the respective precursors as well as during de novo synthesis. The trace chemistry of fire (Bumb et al., 1980) originally developed for the formation of PCDDs/PCDFs is therefore applicable also for combustion processes in the presence of bromine and chlorine: brominated–chlorinated dibenzo-*p*-dioxins (PXDD) and dibenzofurans (PXDF) are formed as trace compounds during combustion processes in the presence of bromine and chlorine.

The final ratio of brominated, brominated–chlorinated and chlorinated aromatics depends on chlorination/bromination reactions and halogen exchange reactions and might finally result in a Br/Cl ratio close to the statistic distribution of chlorine and bromine present in the combusted material, as proposed by laboratory tests (Söderström and Marklund, 2000; Weber et al., 2002b).

The total amount of PBDDs/PBDFs (and PXDDs/PXDFs) formed during thermal processes depends largely on the quality of precursor compounds (Table 2; Fig. 4) and the specific conditions of the thermal treatment (Table 3; Fig. 4). Under thermal stress situations, which may occur in production or recycling processes, precursors which can form PBDDs/PBDFs by a simple elimination step (e.g. PBDE) are potentially relevant in forming PBDDs/PBDFs, while for other BFRs (e.g. TBBP-A and derivatives, aliphatic BFRs), no significant PBDDs/PBDFs formation potential is reported. Under insufficient combustion (e.g. accidental fires, open burning) and pyrolysis conditions in the presence of potent precursors (PBDEs, PBBs and PBP), high amounts of PBDDs/PBDFs can be formed via the precursor pathways.

In contrast, BFRs can be destroyed with high efficiency under controlled combustion conditions, and may then not serve as precursors for PBDDs/PBDFs formation. The similar behaviour of bromine and chlorine under de novo synthesis conditions suggests that the mixed brominated–chlorinated PXDDs/PXDFs are formed in MWI therefore primarily by fly ash catalysed de novo synthesis, similar to the PCDDs/PCDFs. This is supported by the similar isomer distribution patterns of PXDDs/PXDFs and PCDDs/PCDFs found in MWI.

The increased consumption of brominated flame retardants in the last two decades resulted in an increase of bromine in contemporary combustion processes/fires. Therefore, the development of screening tools for brominated and brominated–chlorinated compounds in relevant combustion processes may be important in gaining an overview of the significance of PXDD/PXDF emissions.

¹³ In these tests, the Cu concentration was also increased by the feed of flame retarded printed circuit boards which might have had an impact on increased PCDD/PCDF formation.

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